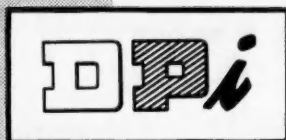


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Address inquiries to
Eastman Organic Chemicals Dept.
Distillation Products Industries
Division of Eastman Kodak Company
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Alkanephosphonic Acids and Derivatives

By HARRY W. COOVER*

This article is a brief summary of the alkanephosphonic acids and their derivatives, that is, those compounds having one carbon-to-phosphorus bond and in which the phosphorus atom is in its pentavalent state.

A scientifically planned study of organophosphorus compounds was first begun in the early part of the nineteenth century. In spite of this, the infrequent references to these compounds in the literature and in standard textbooks show that this branch of organic chemistry has had a rather slow development compared with that of other branches. More recently, however, interest in organophosphorus compounds has been revived. This renewed interest is, no doubt, the direct result of the many valuable uses that are being found for these compounds as solvents, insecticides, plasticizers, stabilizers, and flameproofing agents (1). Recently, several pertinent publications have appeared. The book, "Organophosphorus Compounds," by Kosolapoff (2), and review articles by Atherton (3), Saunders (4), and Martin (5) deserve special mention.

The nomenclature of organophosphorus compounds has been confusing and often inconsistent, but steps are now being taken towards standardization.**

The system followed here is that adopted by *Chemical Abstracts* (6), and a few examples will illustrate its usage. Monobasic organophosphorus acids contain *in* as a part of the suffix. For example, $(\text{CH}_3)_2\text{P}(\text{OH})$ is named dimethylphosphinous acid, and $(\text{CH}_3)_2\text{P}(\text{O})\text{OH}$ is dimethylphosphinic acid. The *ous* and *ic* endings of the suffix indicate, respectively, the trivalent and the pentavalent oxidation states of the phosphorus atom. Dibasic organophosphorus acids contain *on* in the suffix. For example, $\text{CH}_3\text{P}(\text{OH})_2$ is methanephosphonous acid, and $\text{CH}_3\text{PO}(\text{OH})_2$ is methanephosphonic acid.

It should be noted that, in the monobasic acids, the alkyl groups attached to the phosphorus atom are named as such (dimethylphosphinous acid), whereas, in dibasic acids, the alkyl group attached to phosphorus is designated as an alkane (methanephosphonous acid).

The nomenclature of halogen derivatives is exemplified by: $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ —methanephosphonyl dichloride; $(\text{CH}_3)_2\text{P}(\text{O})\text{Cl}$ —dimethylphosphonyl chloride; $(\text{CH}_3\text{O})\text{P}(\text{O})\text{Cl}_2$ —methyl dichlorophosphate; $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{Cl}$ —dimethyl chlorophosphate.

Examples of amide nomenclature are as follows: $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{NHCH}_3)_2\text{-N,N'}$ —dimethylbenzenephosphondiamide; $(\text{C}_6\text{H}_5\text{O})\text{P}(\text{O})(\text{NHCH}_3)_2\text{-phenyl-N,N'}$ —dimethyldiamidophosphate.

The preparation of alkanephosphonic acids and derivatives may be accom-

*Research Laboratory, Tennessee Eastman Company, Kingsport, Tennessee.

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plished by twelve general methods.

I. Oxidation of Primary Phosphines and Derivatives

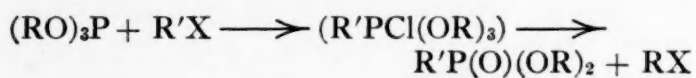
The reaction may be carried out with different oxidizing agents, such as potassium permanganate (7), hydrogen peroxide (8), and fuming nitric acid (9):



This method of preparation is hazardous and difficult to control. All phosphines oxidize quite readily in air.

II. Treatment of an Alkyl Halide with Ester Derivatives of Trivalent Phosphorus

The alkanephosphonic acids and derivatives may be prepared by the following type reaction:



For reactive halides such as methyl iodide, the reaction takes place at room temperature, for example, with triethyl phosphite (10). With the higher-boiling alkyl halides, that is, where $\text{R}'\text{X}$ is higher boiling than RX , the reaction is conveniently carried out by mixing equivalent amounts of reactants in a distillation flask and heating at such a temperature that RX distills from the reaction mixture as it is formed.

The reaction of an alkyl halide and the sodium salt of a dialkyl hydrogen phosphite is carried out by first converting the phosphite to the salt with sodium in an inert solvent, such as ether or benzene, and then adding the alkyl halide. The reactivity of the alkyl halide determines the temperature used.

Generally, only primary unsubstituted alkyl halides have been used, but some notable exceptions indicate that, under the proper conditions, secondary and tertiary alkyl halides may also undergo this reaction (11-16). When the reaction is complete, the precipitated salt is removed by washing, and the product purified by distillation.

Amides of alkanephosphonic acids are

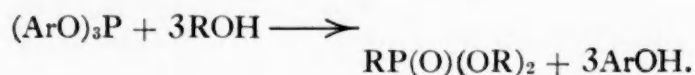
prepared similarly by reacting an alkoxydaminophosphine with an alkyl halide:



The amides may also be prepared from the alkanephosphonic acid chlorides, RPOCl_2 , and ethereal or aqueous solutions of ammonia or amines.

III. Treatment of Triaryl Phosphites with Alcohols

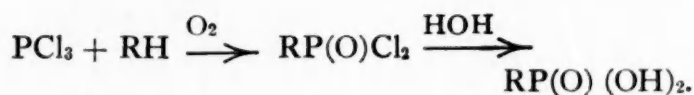
Reaction of triaryl phosphites with alcohols can be carried out by heating the mixture at about 200 C:



The reaction is carried out, preferably, with a substantial excess of the alcohol, and satisfactory amounts of phosphonate are obtained when R is small.

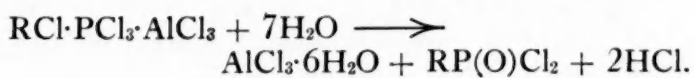
IV. Treatment of Hydrocarbons with Phosphorus Trichloride

The reaction of hydrocarbons with phosphorus trichloride in the presence of oxygen to give alkane- or cycloalkane-phosphonyl dichlorides was discovered recently by Clayton and Jensen (17):



v. Hydrolysis of an $\text{RCl} \cdot \text{PCl}_3 \cdot \text{AlCl}_3$ Complex

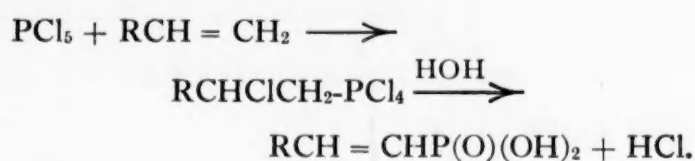
Another very recent method of preparation of alkanephosphonyl dichlorides involves the careful hydrolysis of a complex which has been formulated thus (18):



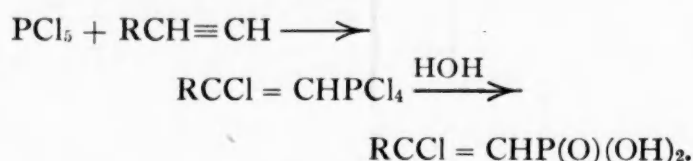
Hydrolysis of alkanephosphonyl dichlorides, RP(O)Cl_2 , by warm water, yields the corresponding phosphonic acids.

VI. Addition of Phosphorus Chlorides to Olefins

Phosphorus pentachloride has been added to olefins to give the corresponding alkanephosphonic acids (19-21):



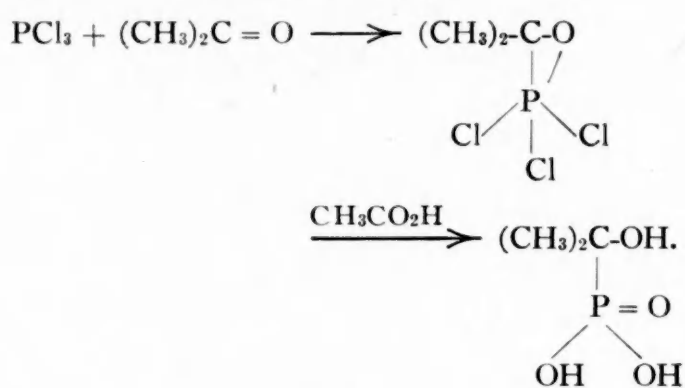
Phosphorus pentachloride adds to mono-substituted acetylenes thus:



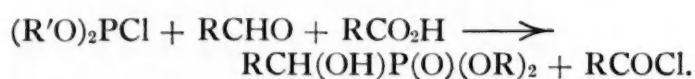
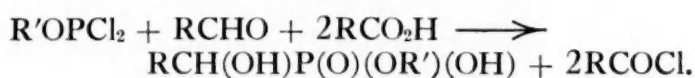
Phosphorus trichloride has been added to olefins in the presence of a peroxide catalyst to give the corresponding chloroalkyldichlorophosphines (22), which are readily oxidizable to the phosphonates.

VII. Addition of Phosphorus Trihalides to Carbonyl Compounds

The addition of halides of trivalent phosphorus to carbonyl compounds is a general method of considerable value for the synthesis of hydroxyalkanephosphonic acids and the compounds readily obtainable therefrom (23):

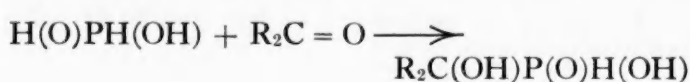


The cyclic intermediate shown above has been proposed, although kinetic studies have shown that the rate of formation of such a cyclic adduct is inconsistent with the observed facts (24). Alkoxy- and dialkoxychlorophosphines also can be added to carbonyl compounds, according to the following equations (25):



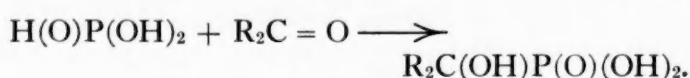
Carbonyl compounds may be treated with phosphorus derivatives containing a real or potential phosphorus-hydrogen bond to yield the corresponding hydroxy-

substituted derivatives. For example, hypophosphorus acid adds to aldehydes and ketones to give the corresponding hydroxyalkylphosphinic acid (26):



which may be oxidized to the corresponding hydroxyalkanephosphonic acid.

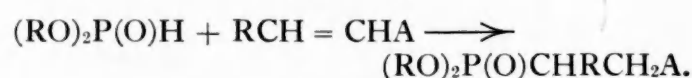
Reactions with phosphorous acid yield hydroxyalkanephosphonic acids directly:



The reaction is conducted by heating the reactants on a water bath for a long period of time, frequently several days.

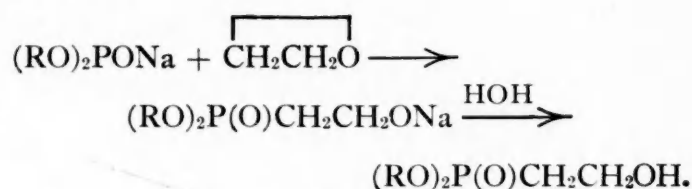
VIII. Addition of Dialkyl Hydrogen Phosphonates with Activated Double Bonds

Activated double bonds have been recently reported to undergo an addition reaction with dialkyl hydrogen phosphonates, as shown in the following equation, where A is $\text{C}\equiv\text{N}$, COOR , or a similar activating group (27):



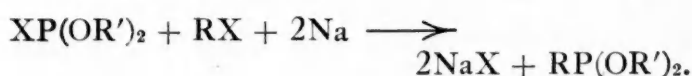
IX. Treatment of Olefin Oxides with Sodium Dialkyl Phosphites

Reaction of sodium dialkyl phosphites with ethylene oxide yields, on acidification, the dialkyl hydroxyalkanephosphonate (28):



X. Reactions of the Wurtz Type

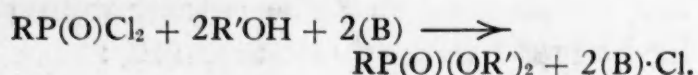
The Wurtz-type reaction with phosphorus halides has been reported (29):



XI. Treatment of Alkanephosphonyl Dichlorides with Alcohols and Phenols

Alkanephosphonyl dichlorides may be converted to esters by reaction with the desired alcohol, or phenol, in the presence of the theoretical amount of a ter-

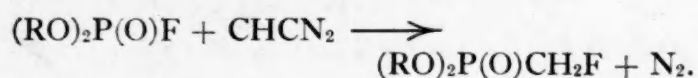
tiary amine (B), such as pyridine or a dialkylaniline (30, 31):



Hydrolysis of phosphonic esters by hot hydrochloric or hydrobromic acid yields the free phosphonic acid. With concentrated acids, the ester group is eliminated as an alkyl halide.

XII. Treatment of Trialkyl Halophosphates with Diazomethane

Reaction of a halophosphate with diazomethane yields the corresponding halophosphonate (32):



The physical and chemical properties of alkanephosphonic acids and derivatives are analogous to those of the alkane-sulfonic acids and derivatives. The alkanephosphonic acids are solids and the lower members are deliquescent. They are among the most thermally stable derivatives of phosphorus. On strong heating, some anhydride formation takes place, but only heating to very high temperatures cleaves the carbon-phosphorus bond. The esters are high-boiling liquids of pleasant odor and may be used as alkylating agents. The simple dialkylamides of alkanephosphonic acids are colorless oils, which dissolve easily in alcohol or ether, but sparingly in water.

It has been generally noted that the organic compounds of nitrogen, sulfur, and arsenic can be related directly to the organophosphorus compounds. In this respect, the nitrogen-phosphorus analogy is closer in the trivalent phosphorus compounds, which have the free electron pair; on the other hand, the sulfur-arsenic-phosphorus analogy is closer in the pentavalent phosphorus compounds.

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